Journal of Chemical Physics 2010 vol.132 N9

Features of polymer chain dynamics as revealed by intermolecular nuclear magnetic dipole-dipole interaction: Model calculations and field-cycling NMR relaxometry

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Abstract

Proton NMR phenomena such as spin-lattice relaxation, free-induction decays, and solid echoes are analyzed with respect to contributions by intermolecular dipole-dipole interactions in polymer melts. The intermolecular dipole-dipole correlation function is calculated by taking into account the correlation hole effect characteristic for polymer melts. It is shown that the ratio between the intra- and intermolecular contributions to NMR measurands depends on the degree of isotropy of chain dynamics anticipated in different models. This, in particular, refers to the tube/reptation model that is intrinsically anisotropic in clear contrast to n -renormalized Rouse models, where no such restriction is implied. Due to anisotropy, the tube/reptation model predicts that the intramolecular contribution to the dipole-dipole correlation function increases with time relative to the intermolecular contribution. Therefore, the intramolecular contribution is expected to dominate NMR measurands by tendency at long times (or low frequencies). On the other hand, the isotropic nature of the n -renormalized Rouse model suggests that the intermolecular contribution tends to prevail on long-time scales (or low frequencies). Actually, theoretical estimations and the analysis of experimental spin-lattice relaxation data indicate that the intermolecular contribution to proton NMR measurands is no longer negligible for times longer than 10 -7s- 10-6s corresponding to frequencies below the megahertz regime. Interpretations not taking this fact into account need to be reconsidered. The systematic investigation of intermolecular interactions in long-time/low frequency proton NMR promises the revelation of the dynamic features of segment displacements relative to each other in polymer melts.

http://dx.doi.org/10.1063/1.3336832